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In-situ and post-cure surface modification of PDMS elastomers for low surface energy applications

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Raymond S. Campos, Sean M. Ramirez, James F. Reuther, Kevin R. Lamison, Bruce M. Novak

5d. PROJECT NUMBER

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14. ABSTRACT

Strategies aimed at promoting the formation of close-pack assemblies of fluoroalkyl helices on the surface of PDMS networks will be described and compared. Fluoroalkyl moieties were incorporated into Pt-catalyzed hydrosilylation networks *in situ* by using vinyl additives possessing either a single fluoroalkyl substituent, $CH2=CH-(CF_2)_7CF_3$ (F8-vinyl), or eight ((methyl, vinyl)D_1(F8H2)$_8T_8$ POSS or vinyl fluorodecyl POSS). Post-cure methods involving the incorporation of surface thiol groups and subsequent thiolene addition reactions were also explored for the facile production of PDMS networks with oleophobic surface properties. Synthetic routes and characterization of intermediates will be presented in addition to dynamic wettability analysis of modified PDMS networks.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
					Joseph Mabry
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Prescribed by ANSI Std. 239.18

In-situ and post-cure surface modification of PDMS elastomers for low surface energy applications

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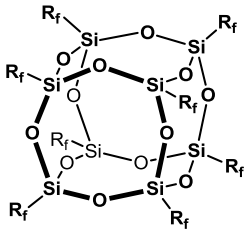
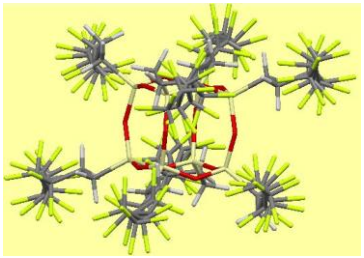
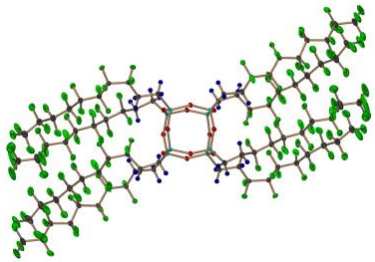
***** Air Force Research Laboratory, Space & Missile Propulsion Division, Edwards Air Force Base, CA 93524**

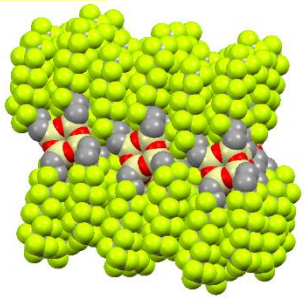
Properties of Fluorodecyl$_8$T$_8$ POSS



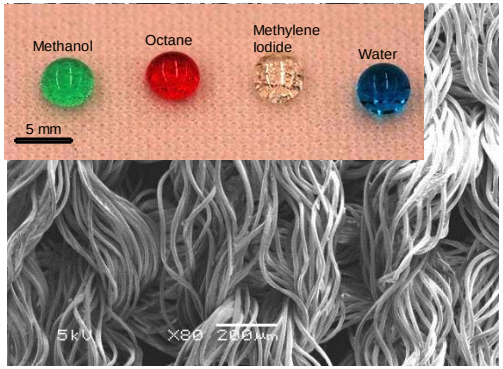


- Extremely low surface energy
- Surface migration in polymers
- Surface responsive behavior



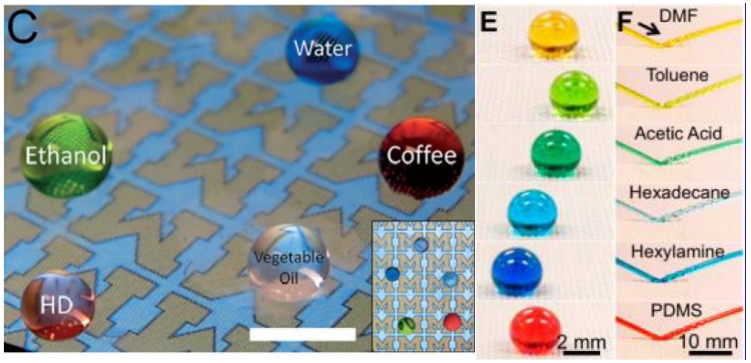


Enabling….



Superomniphobic fabrics via dip-coating

Choi *et al., Ang. Chem.*, 2009

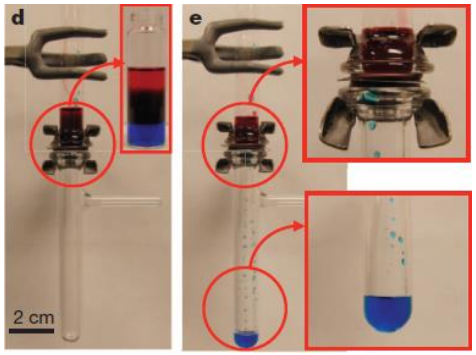


Transparent Omniphobicity

Golovin *et al., Ang. Chem.*, 2013

Extreme Omniphobicity

Pan *et al., JACS.*, 2012

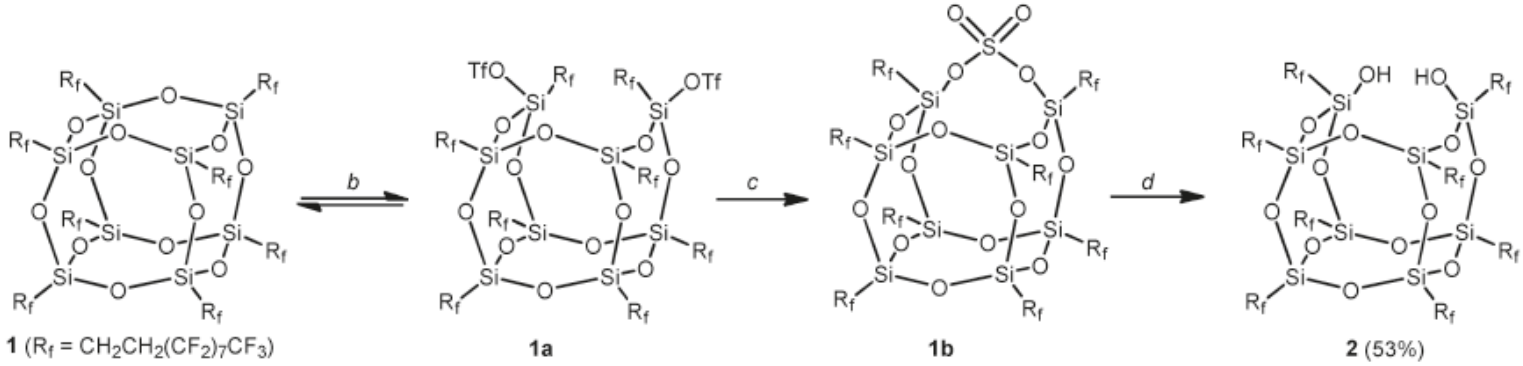


Oil/water emulsion gravity seperation

Kota *et al., JACS.*, 2012

Functional Fluorodecyl POSS Compounds Enabled by Incompletely Condensed Intermediate

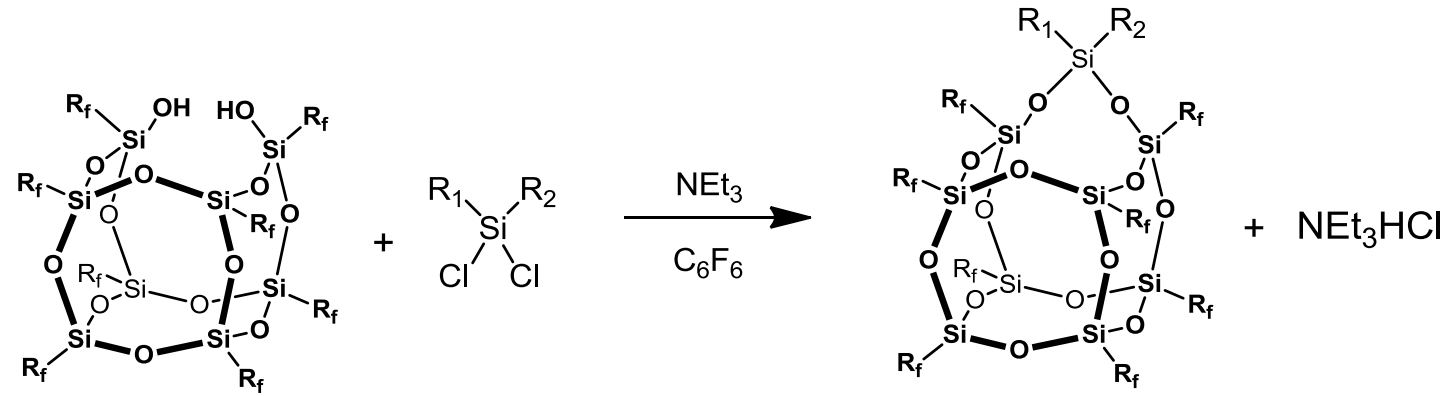
Scheme 1. Synthesis of Incompletely Condensed Fluoroalkyl Silsesquioxane[a]



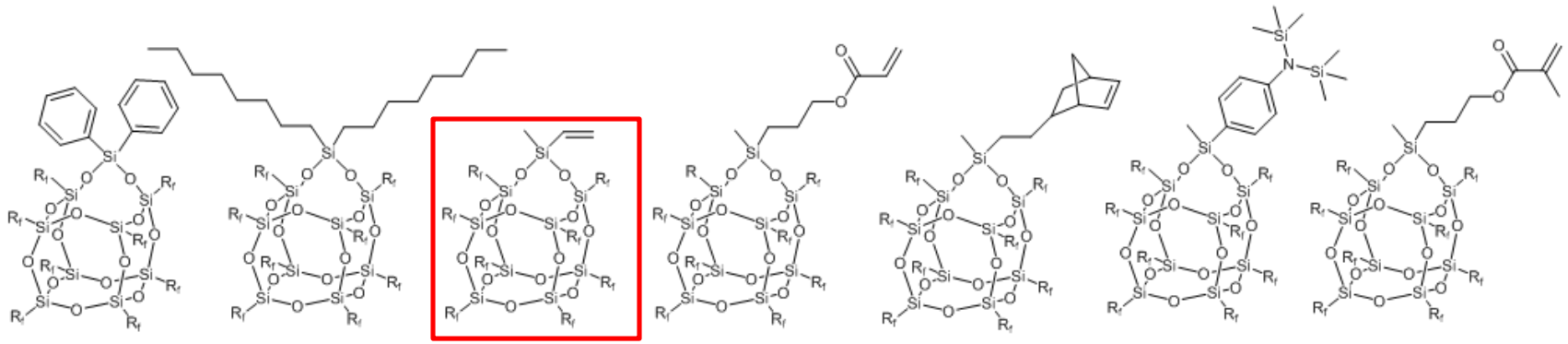
[a] Conditions: All reactions were performed in C_6F_6 at 25 °C. [b] CF_3SO_3H, 75 min; [c] $NBut_4HSO_4$, 30 min; [d] $(CF_3)_2CH_2OH/H_2O$ (10:1), 12 h.

Ramirez, S. M., Diaz, Y. J., Campos, R., Stone, R. L., Haddad, T. S., Mabry, J. M. *JACS,* **2011**, *133*, 20084.

Functional Fluorodecyl POSS Synthesis from Incompletely Condensed Fluorodecyl POSS

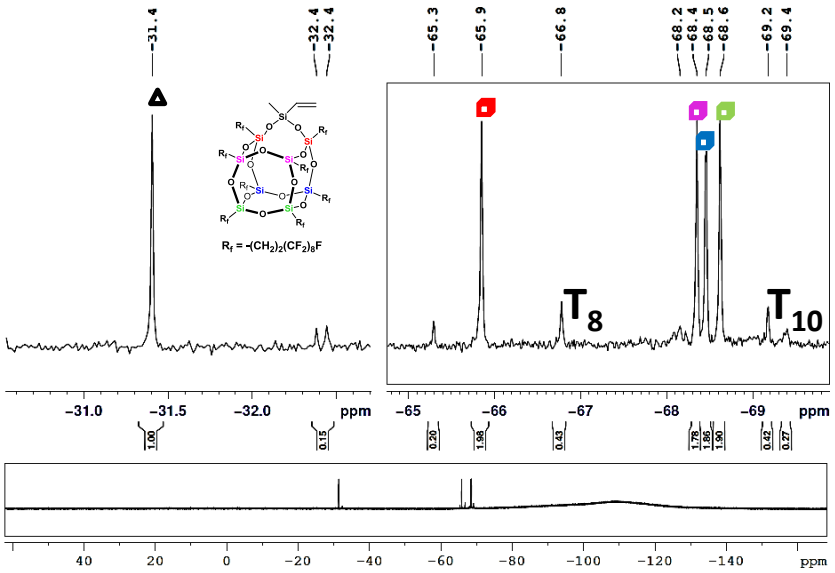


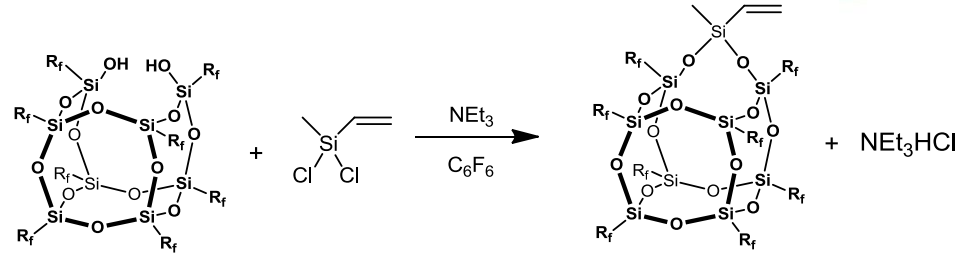
$R_f = -(CH_2)_2(CF_2)_8F$ $R_f = -(CH_2)_2(CF_2)_8F$



Ramirez, S. M., Diaz, Y. J., Campos, R., Stone, R. L., Haddad, T. S., Mabry, J. M. *JACS,* **2011**, *133*, 20084.

Fluorodecyl$_8$T$_8$D$_1$(methyl, vinyl) POSS



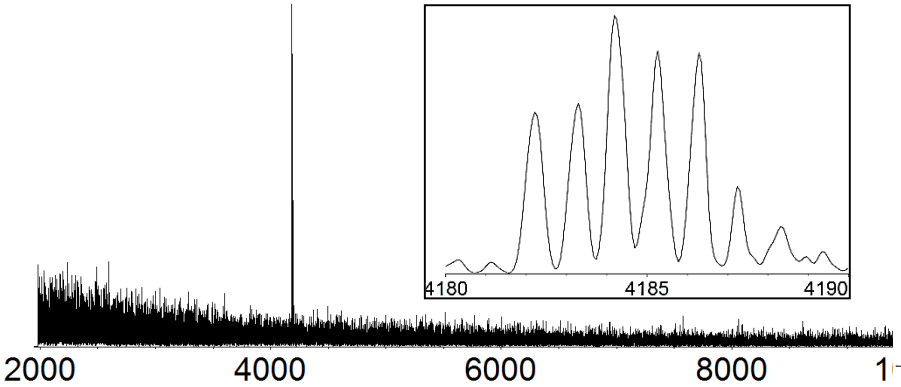


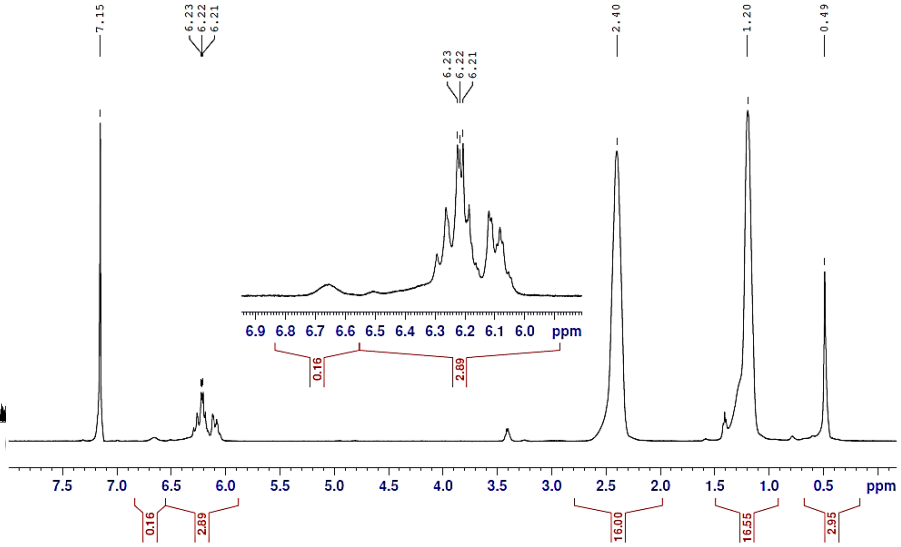
R_f = -(CH$_2$)$_2$(CF$_2$)$_8$F

R_f = -(CH$_2$)$_2$(CF$_2$)$_8$F

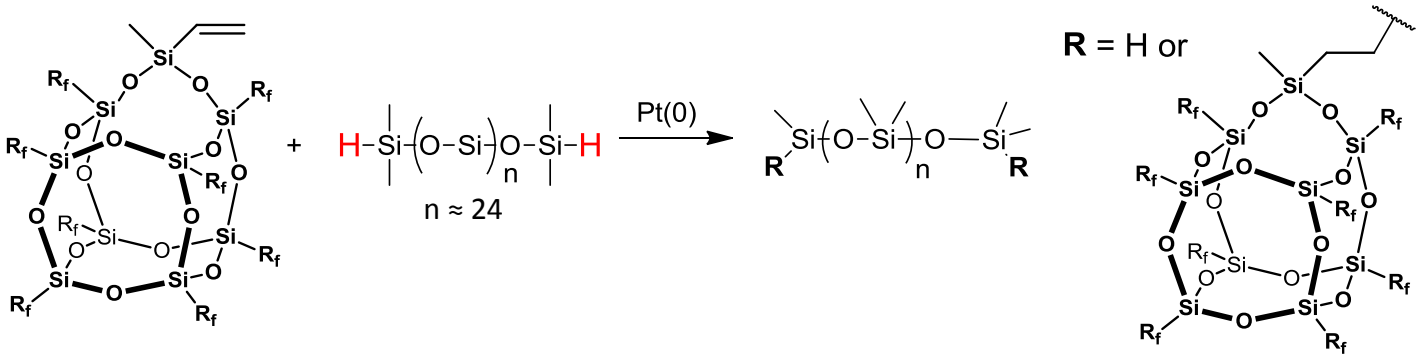
Vinyl F-POSS

Theoretical [M·Ag]$^+$ = 4185.71 Da



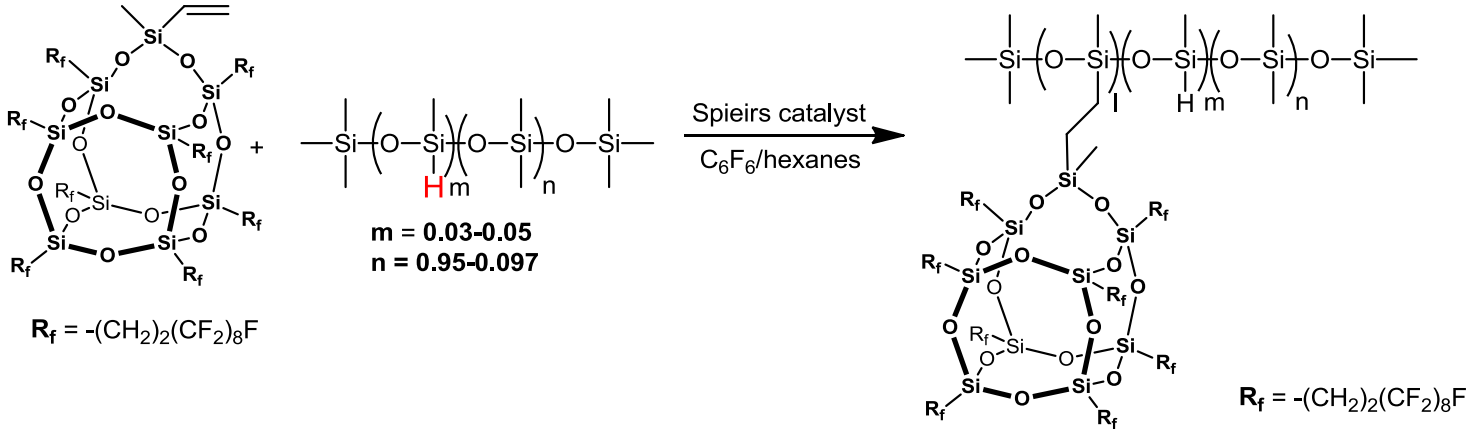


Facile F-POSS Grafting to PDMS via Hydrosilylation

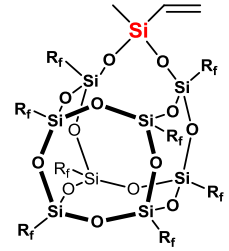


1, 5, 10, 20, 44 wt%

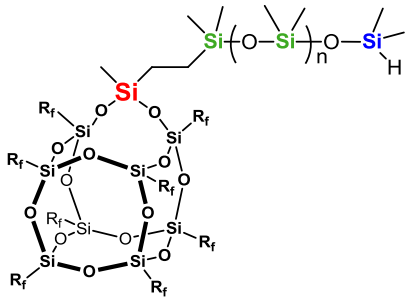
Vinyl: silane, 1:32, 1:8, 1:4, 1:2, 1:1



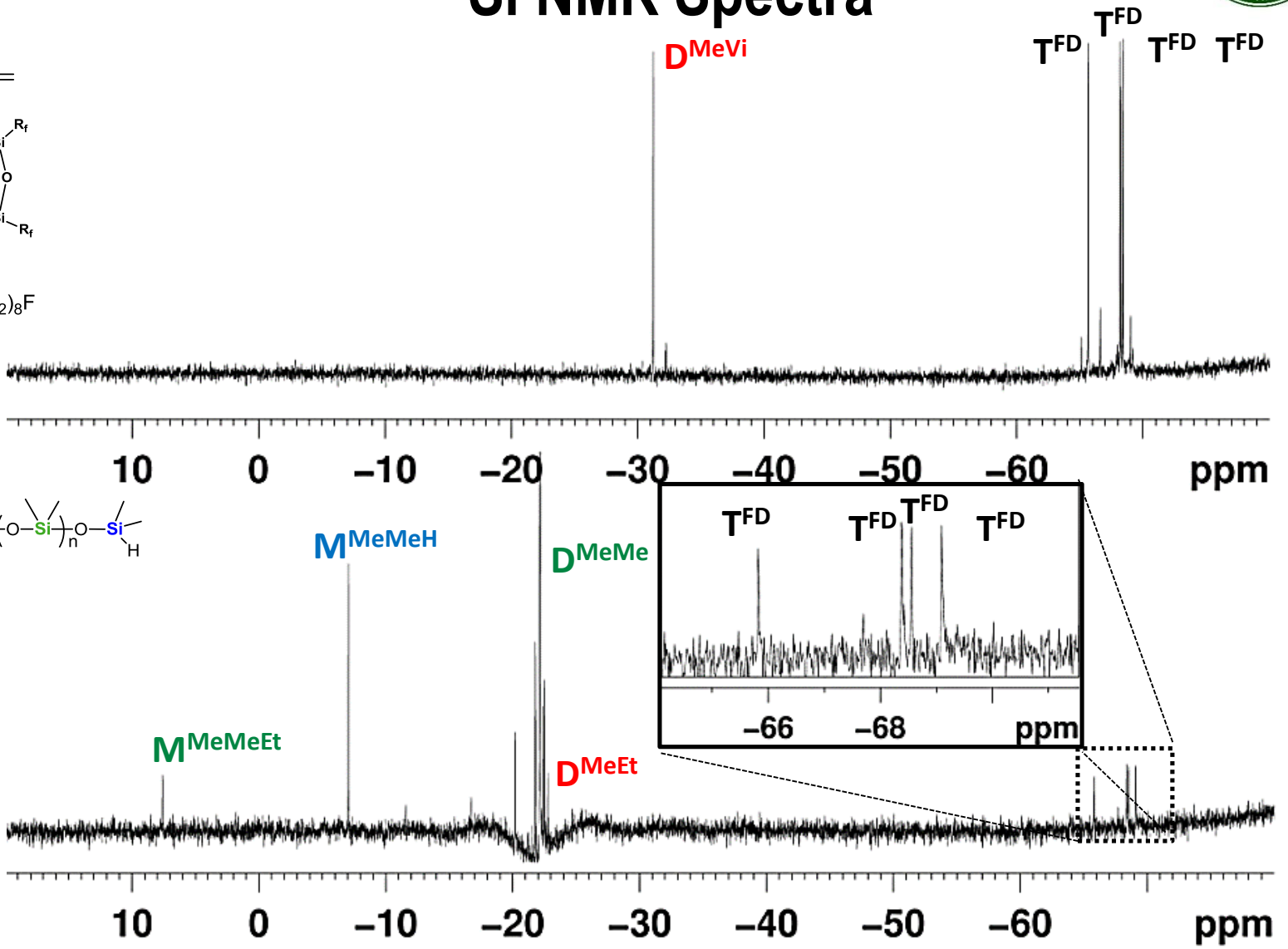
Complete Conversion at 10 wt% F-POSS: ^{29}Si NMR Spectra



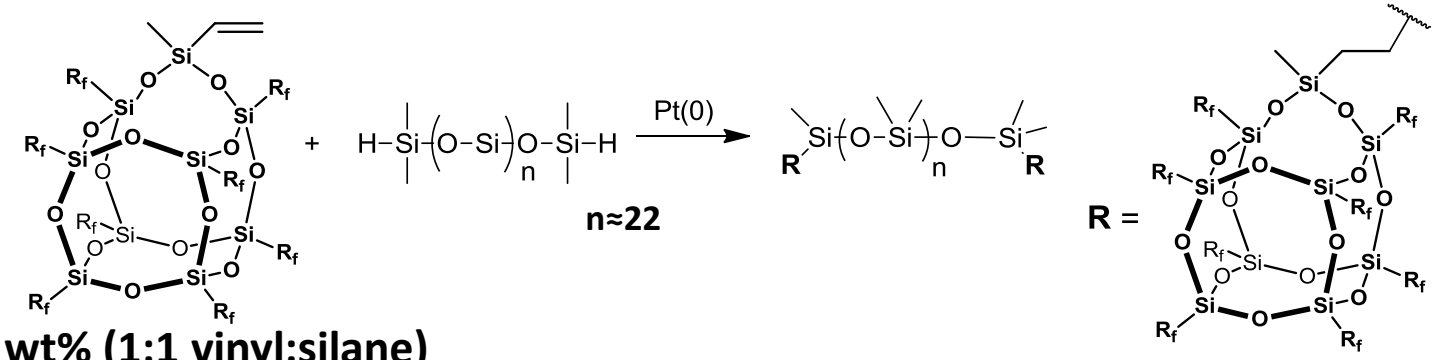
R_f = -$(CH_2)_2(CF_2)_8F$



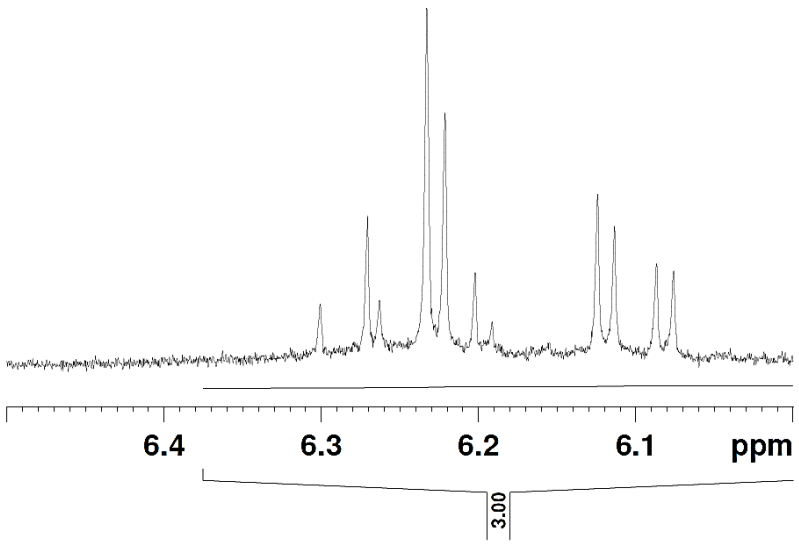
R_f = -$(CH_2)_2(CF_2)_8F$

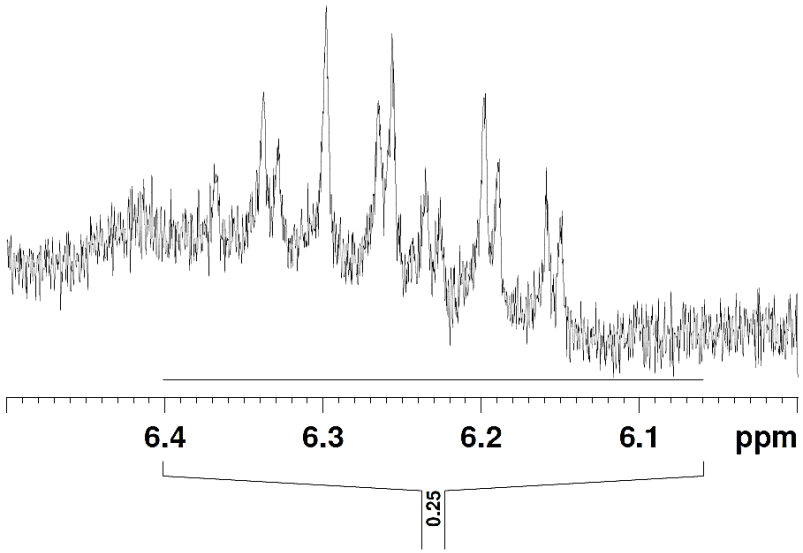


Incomplete Conversion at ≥20 wt% F-POSS: ^{1}H NMR Spectra

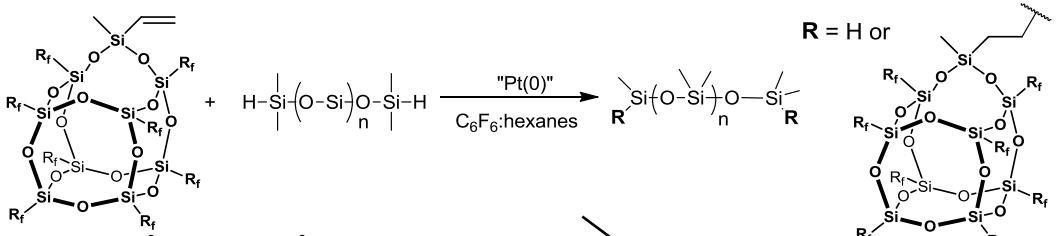


44 wt% (1:1 vinyl:silane)



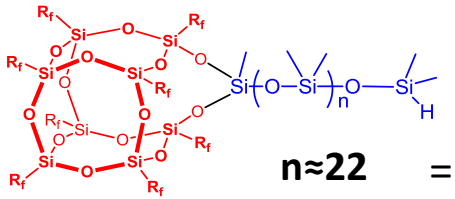


F-POSS PDMS Amphiphile Aggregation



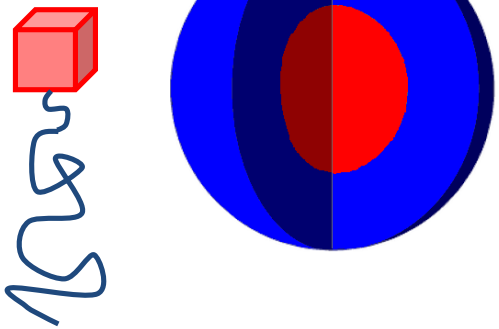
44 wt% (2 mol eq.)

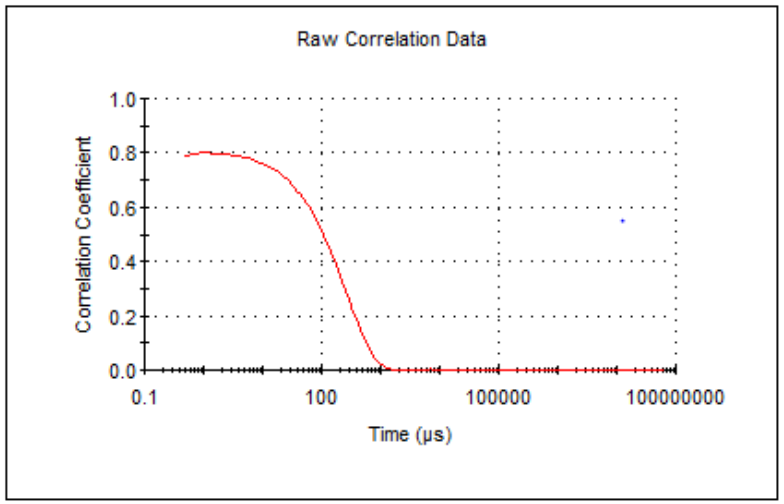
Crude rxn. mix.
4:1 C_6F_6:hexanes

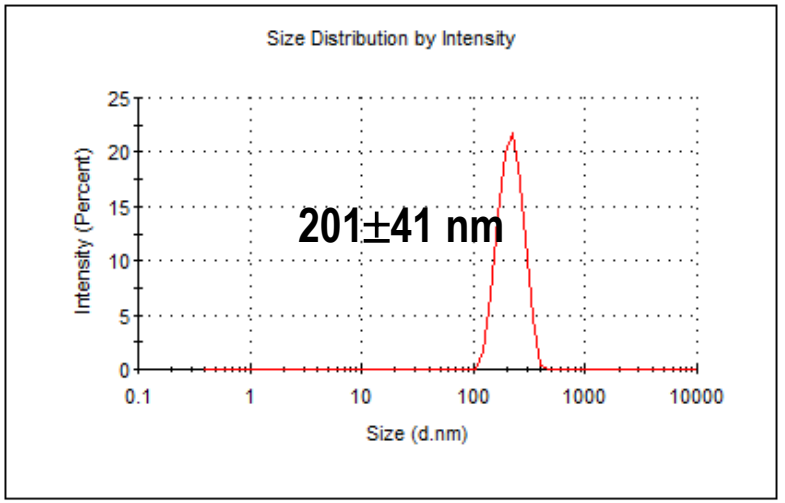


R_f = $-(CH_2)_2(CF_2)_8F$

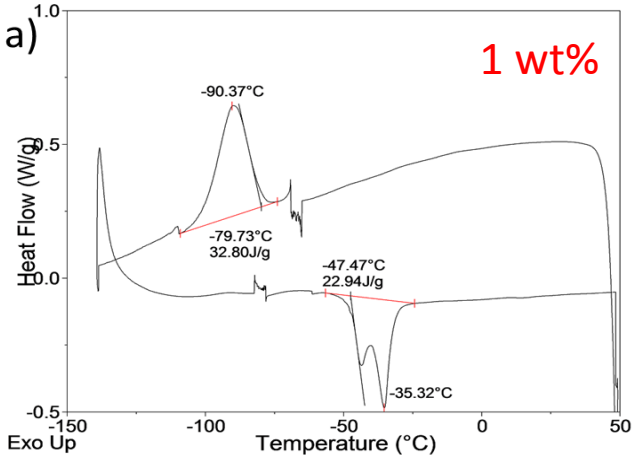
n≈22 =

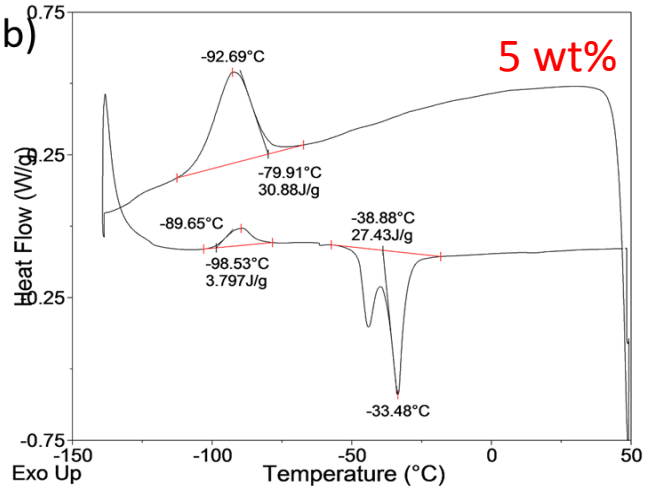


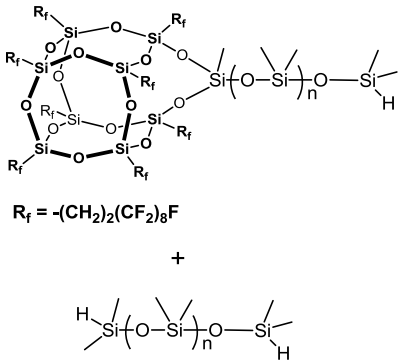


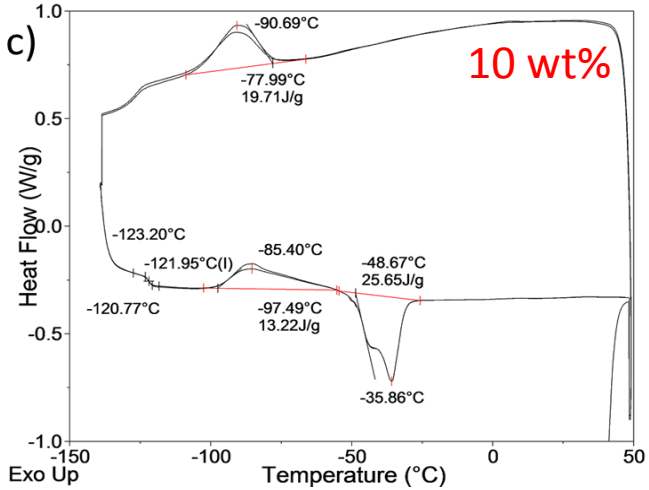


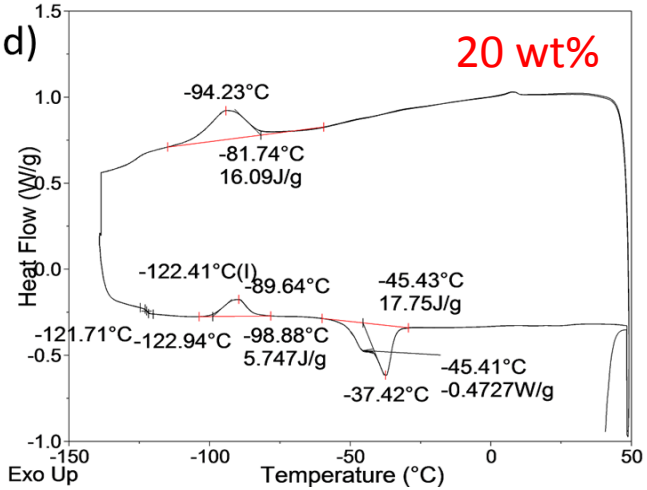
F-POSS Enchainment does not Change the T_g of PDMS



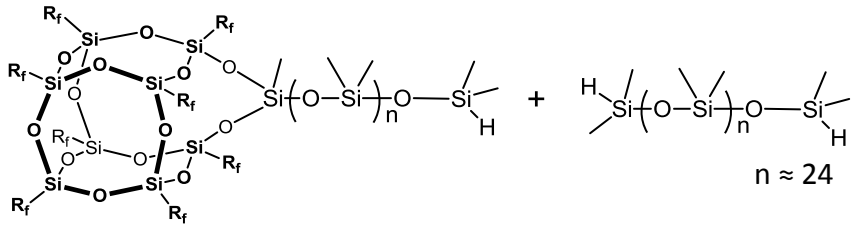




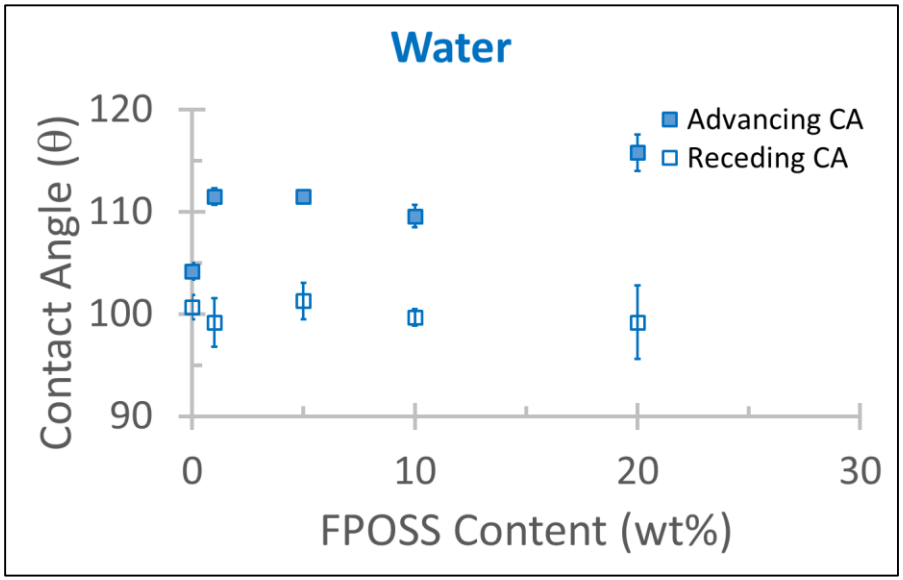


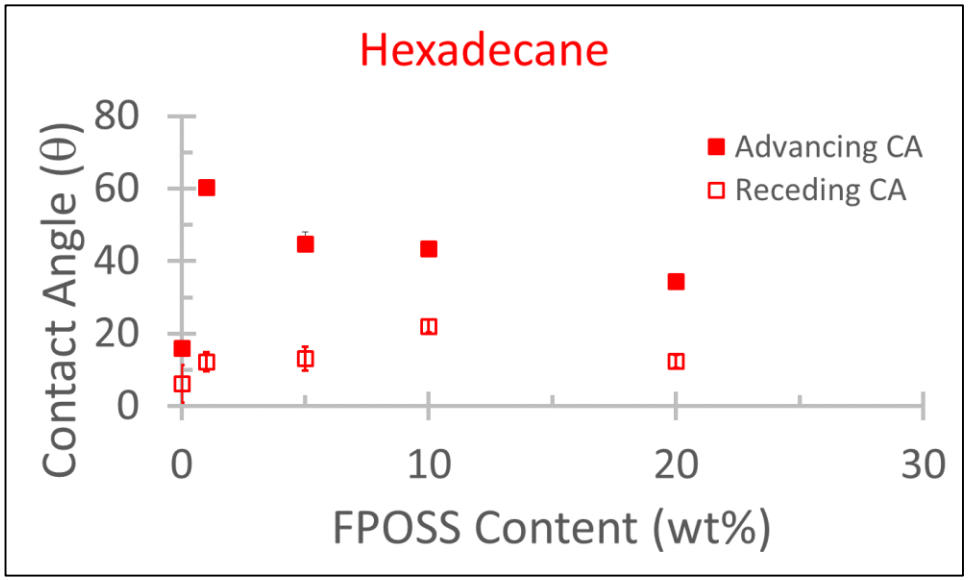


Surface Wetting of Fluorodecyl POSS -PDMS Amphiphiles



$R_f = -(CH_2)_2(CF_2)_8F$

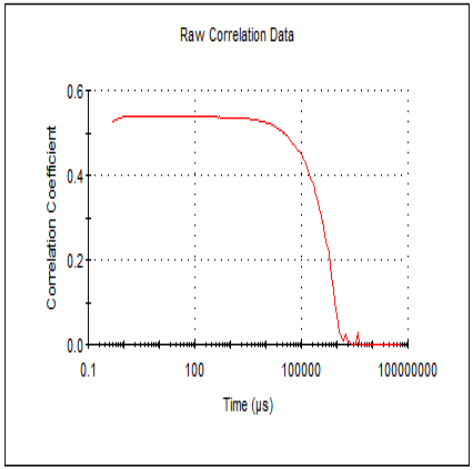


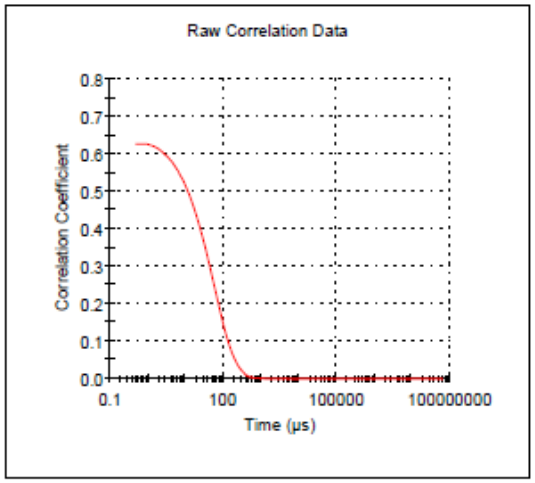


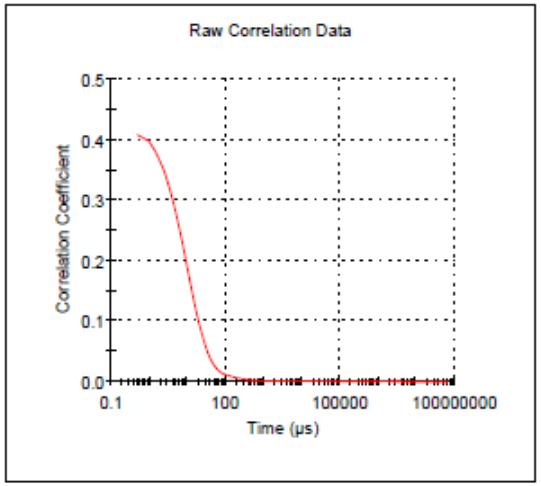
Pure fluorodecyl$_8$T$_8$ POSS: Water $\theta_{adv}/\theta_{rec}$ = 124°/116°

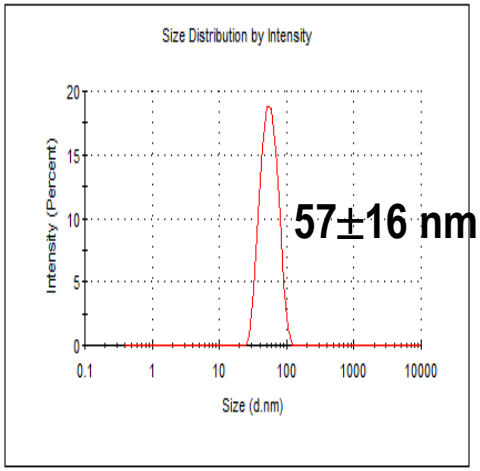
Hexadecane $\theta_{adv}/\theta_{rec}$ = 80°/61°

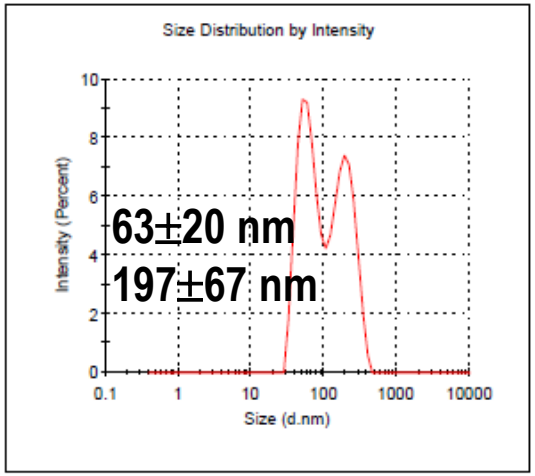
F-POSS PDMS Amphiphile Aggregation: Dynamic Light Scattering

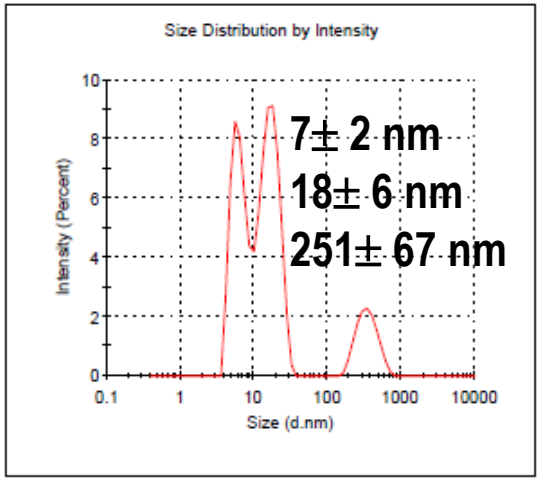










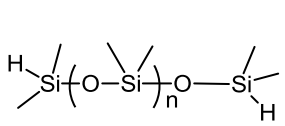


PDMS (1000 cSt)
0.001 M, 25 C

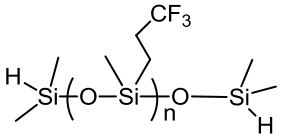
CDCl3
0.001 M, 25 C

AK225
0.001 M, 25 C

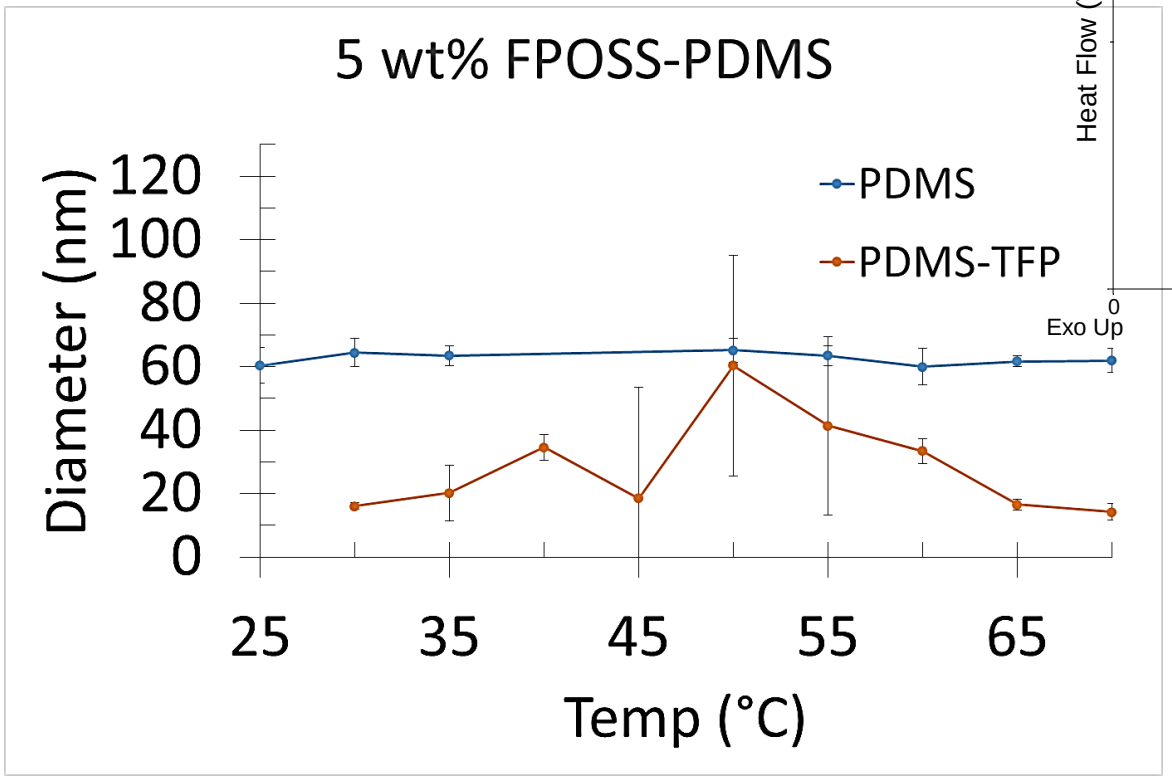
Thermal Stability of FPOSS-PDMS Micelles

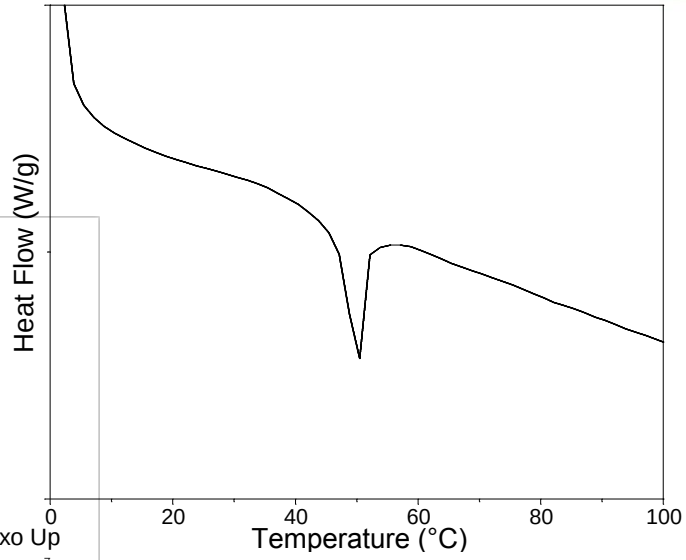


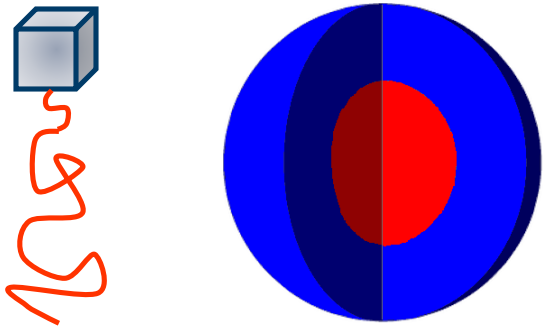
PDMS



PDMS-TFP

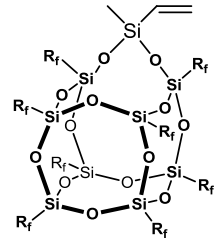






In fluorinated matrix

Surface Wetting of Fluorodecyl POSS-Enchained PDMS Elastomers

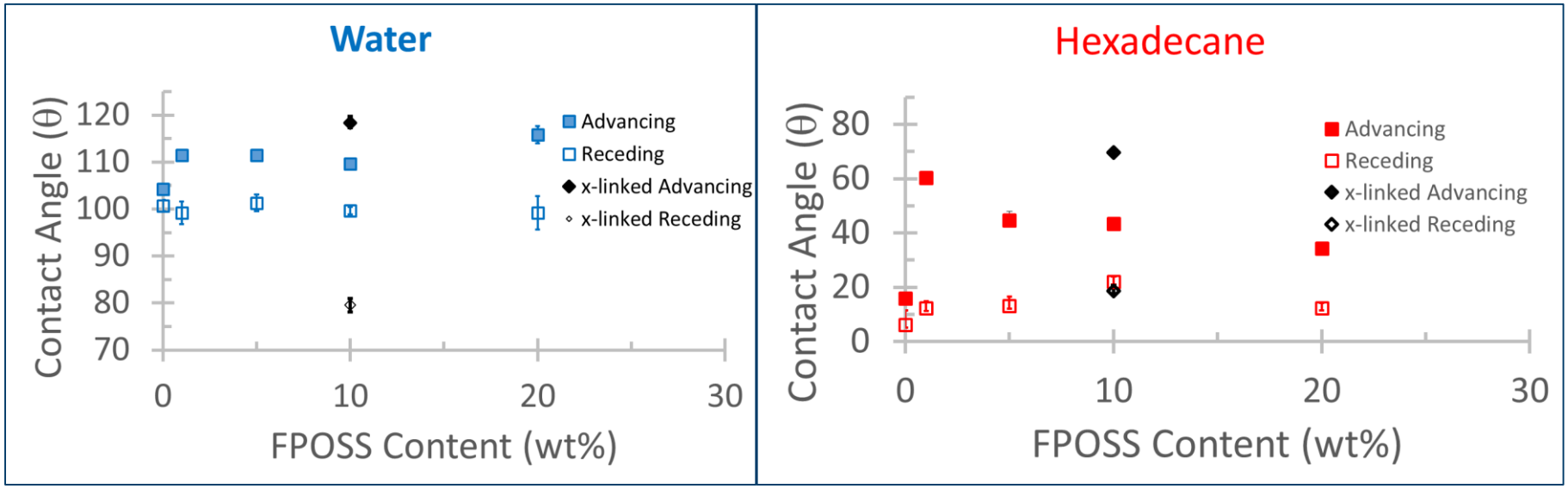


R_f = -$(CH_2)_2(CF_2)_8F$

+ Sylgard 184
10:1 base:curative

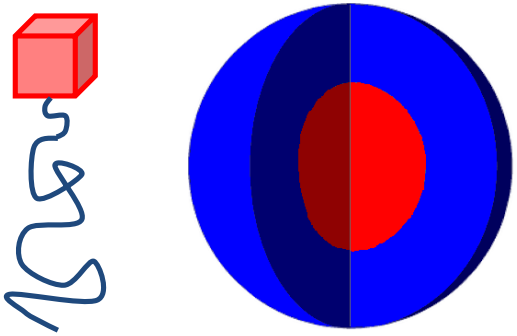
70 °C/4 hrs,
45 °C/17 hrs

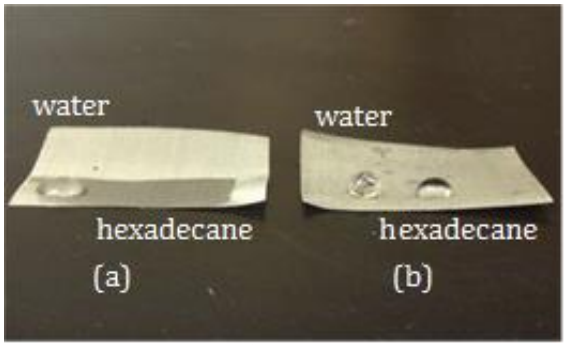
F-POSS enchained PDMS Elastomer
(**Black diamonds in figures**)



Pure fluorodecyl$_8T_8$ POSS: Water $\theta_{adv}/\theta_{rec}$ = 124°/116°
Hexadecane$\theta_{adv}/\theta_{rec}$ = 80°/61°

Summary and Outlook





- FPOSS enchainment enhances mechanical robustness accompanied by a reduction in liquid repellence
- F-POSS end-capped PDMS amphiphiles strongly favor the formation of micelles
- Aggregation plays a large role in the synthesis, assembly, and function of F-POSS PDMS amphiphiles

Stainless steel mesh (325)

H_2O $\theta_{adv}/\ \theta_{rec}$ = 132.6° ± 0.9/ 25.8° ± 9.2
$C_{16}H_{34}$ $\theta_{adv}/\ \theta_{rec}$ = 0°/ 0°

Stainless steel mesh (325) dip-coated 44 wt% FPOSS x-linked PDMS

H_2O $\theta_{adv}/\ \theta_{rec}$ = 154.7 ± 3.5°/147.8 ± 1.7°
$C_{16}H_{34}$ $\theta_{adv}/\ \theta_{rec}$ = 128.1 ± 1.1°/ 84.0 ± 20.7°

Acknowledgments